METHOD FOR PRODUCING TITANIA-DOPED FUSED SILICA GLASS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates generally to methods for producing doped glass. More specifically, the invention relates to a method for producing a titania-doped fused silica glass and a titania-doped fused silica glass having low water content.

5   ### 2. Background Art

Extreme ultraviolet (EUV) lithography is emerging as one of the next-generation lithography techniques that will allow high-volume production of integrated circuits with sub-100-nm features. EUV lithography as currently contemplated involves producing electromagnetic radiation at around 13 nm. The EUV radiation may be produced, for
10 example, using a 1064-nm neodymium-YAG laser which produces a xenon gas plasma or from a synchrotron source. A condenser collects the EUV radiation and projects it onto a mask containing a pattern to be replicated on a silicon wafer. The mask reflects the EUV radiation into an imaging system, which then projects an image onto a resist-coated silicon wafer. The pattern is later transferred to the silicon wafer by etching.

The mask structure consists of a substrate ("mask blank"), a reflective multilayer
15 stack formed on the mask blank, and an absorber formed on the multilayer stack. Typically, the multilayer stack includes alternating layers of Mo and Si or Mo and Be. The absorber defines the pattern to be replicated on the silicon wafer. The mask blank may be made of silicon or glass or other suitable material. It is important that the mask blank has a low
20 thermal expansion so that it does not distort under exposure to the EUV radiation. Titania-doped fused silica (SiO_2-TiO_2) is one example of a glass that can be made to have a very low thermal expansion, $i.e.$, lower than pure fused silica with the potential for a coefficient of thermal expansion that approximates zero. The coefficient of thermal expansion of the SiO_2-TiO_2 glass can be controlled by adjusting the percent weight content of TiO_2 in the glass.

25 Commercial processes for producing SiO_2-TiO_2 glass involve transporting a mixture of a silica precursor and a titania precursor to a reaction site, thermally decomposing the mixture of precursors (usually via flame hydrolysis) into SiO_2-TiO_2 particles ("soot"), and depositing the soot on a support. In the conventional boule process, the soot is captured in a

cup of a refractory furnace at consolidation temperatures (typically 1200 to 1900°C) so as to allow the soot to immediately consolidate into a solid body ("boule"). These high consolidation temperatures may result in compositional variations within the glass, which would result in the glass having non-uniform thermal expansion properties. Applications such as EUV lithography require very low variations in coefficient of thermal expansion (CTE) within the substrate (e.g., 0 ± 5 ppb/°C). Therefore, a production method which favors homogeneity in the SiO_2-TiO_2 glass is desirable.

For environmental reasons, commercial processes for producing SiO_2-TiO_2 glass use a chloride-free material such as octamethylcyclotetrasiloxane (OMCTS), a siloxane, as a silica precursor. Usage of organic precursors and a hydrogen-containing fuel for thermal decomposition of the organic precursors inherently results in the SiO_2-TiO_2 glass containing more OH (often referred to as water) than can be tolerated by infrared transmission applications or deep-UV applications such as at 157 nm. In particular, OH has some absorption at these wavelengths. Therefore, a production method which favors dehydration of the SiO_2-TiO_2 glass is also desirable.

SUMMARY OF THE INVENTION

In one aspect, the invention relates to a method for producing a fused silica glass containing titania. The method comprises synthesizing particles of silica and titania by delivering a mixture of a silica precursor and a titania precursor to a burner, growing a porous preform by successively depositing the particles on a deposition surface while rotating and translating the deposition surface relative to the burner, consolidating the porous preform into a dense glass.

Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic of a system for producing SiO2-TiO2 glass in accordance with one embodiment of the invention.

Figure 2 is a top view of a mask blank.

Figure 3 is a side view of the mask blank shown in Figure 2.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the invention provide a method for producing SiO_2-TiO_2 glass substrates with low variations in CTE within the substrate. The method involves transporting silica and titania precursors in vapor form to deposition burners. The precursors exit the

5 deposition burners where they react to form fine SiO_2-TiO_2 particles ("soot"). The soot collect on a deposition surface to form a porous preform. The method further includes consolidating the porous preform to give a dense SiO_2-TiO_2 glass in a separate step. Consolidating the glass in a separate step eliminates the need to capture the soot at consolidation temperatures. This allows the soot to be deposited at lower temperatures

10 (typically, 200°C to 500°C lower) than possible with the conventional boule process. SiO_2-TiO_2 glass having low OH content can be produced by exposing the preform to a dehydrating agent, such as chlorine or fluorine, prior to consolidation. Chlorine and/or fluorine treatment would also remove impurities from the glass which could result in seeds.

In one embodiment of the invention, production of SiO_2-TiO_2 glass follows the same

15 basic procedure as a conventional vapor-axial deposition (VAD) process, except that two delivery systems are needed to provide entrained vapors of titania precursor and silica precursor. The two separate vapor trains feed into a manifold where they are mixed together. The mixture is then carried through fume lines to deposition burners where it reacts to form soot. The soot is deposited on a bait which is rotated and moved axially within an enclosure.

20 The porous preform formed by the soot is thermally consolidated into dense glass in a separate step. An intermediate chlorine and/or fluorine treatment step may be used to remove impurities or adsorbed water from the glass. Relatively large homogeneous SiO_2-TiO_2 glass substrates, e.g., 6" x 6" x 0.25" substrates and larger, can be made using this process.

Figure 2 is a schematic of a system, generally designated by the numeral 2, for use in

25 practicing the present invention. The system 2 includes source 4 of a silica precursor 6. There are many choices available for the silica precursor, e.g., a siloxane such as OMCTS ($Si_4O_4(CH_3)_8$), halogen-based precursors such as silicon tetrachloride ($SiCl_4$), silane (SiH_4), and other silicon-containing compounds. In general, halogen-free precursors are preferred because they are more environmentally friendly. Silane exists in vapor form at room

30 temperature and does not need a vaporization step prior to mixing with the titania precursor. The silica precursor 6 is pumped into the source 4 at a predetermined rate. The source 4, which may be a vaporizer or evaporator tank or similar equipment, converts the silica precursor 6 into vapor form if the silica precursor 6 is not already in vapor form. An inert

carrier gas **8**, *e.g.*, nitrogen, carries the silica precursor **6** vapors through a distribution system **12** to a manifold **14**. A stream of inert gas **10**, *e.g.*, nitrogen, is brought into contact with the silica precursor **6** vapors to prevent saturation.

5   The system **2** further includes a source **16** of the titania precursor **18**, *e.g.*, a titanium alkoxide such as titanium isopropoxide ($Ti(OPri)_4$). The titania precursor **18** is pumped into the source **16** at a predetermined rate. The source **16** converts the titania precursor **18** into vapor form if the titania precursor **18** is not already in vapor form. A stream of inert gas **22**, *e.g.*, nitrogen, can be brought into contact with the vaporous titania precursor to prevent saturation of the vapors. An inert carrier gas **20**, *e.g.*, nitrogen, entrains the titania precursor

10   **18** vapors and carries the vapors through a distribution system **24** to manifold **14**, where they are mixed with the silica precursor **6** vapors. The mixture of vaporous precursors passes through heated fume lines **26** to deposition burners **28** positioned below a multi-chambered hood **32**. The temperatures of the fume lines **26** are preferably controlled to prevent reaction prior to reaching the deposition burners **28**.

15   Prior to injecting the mixture into the deposition burners **28**, a bait **34** is disposed in the center chamber **33** of the multi-chambered hood **32**. Typically, the bait **34** is made of fused quartz. However, the bait **34** may also be made of other bait materials such as alumina or graphite. Further, the bait **34** may be shaped like a rod, as shown in the drawing, or may have other desired shape. For example, the bait **34** may be shaped like a ball or a plate. The

20   upper end of the bait **34** is connected to a spindle **36**, for example, by pin **35**. The spindle **36** is in turn connected to a drive motor **38**. When the drive motor **38** is energized, the spindle **36** and the bait **34** rotate in unison and ascend within the chamber **33** at predetermined speeds. The speed at which the bait **34** ascends is critical to the temperature profile and shape of the porous preform **40** formed on the bait **34**. A typical bait speed is 0.3 to 0.5 mm/min.

25   Burner placement is fixed and bait speed is adjusted to maintain a constant burner-to-soot preform distance during deposition. Although two deposition burners **28** are shown, it should be clear that one or more than two deposition burners can be used. In general, the number of deposition burners will depend on the size of porous preform to be made. The deposition burners **28** are typically inclined at an angle with respect to the translation axis of

30   the bait **34**. Auxiliary heat burners **29** may also be provided to promote the thermal environment needed to form the SiO_2-TiO_2 particles. Improper placements of the deposition burners **28** and the auxiliary heat burners **29** could result in both excessively hot and cold regions on the preform. The occurrence of these will cause unwanted effects on the density, shape, deposition efficiencies, and other related defects of the preform.

The mixture of vaporous precursors are injected into the deposition burners **28**, as previously described. The vaporous precursors exit the deposition burners **28** where they react to form SiO_2-TiO_2 soot. The soot is formed by hydrolysis or thermal oxidation reaction of the precursors with a methane-oxygen flame. Alternatively, an oxyhydrogen flame could

5 be used to form the soot. The soot is deposited on the lower end of the bait **34** to form a columnar porous preform **40**. The lower end of the bait **34** on which the preform is formed is generally spherical in shape but could be planar or have other shape. The perform **40** grows as more soot is deposited and the bait **34** ascends. Spurious soot is generated at the time of deposition and is removed through the exhaust chambers **42**. The chamber **33** in which the

10 spindle **36** and bait **34** travel is provided with a stream of clean air **44** that is directed towards the emerging preform **40**. This stream of air **44** directs the spurious soot outward and away from the preform **40** into the exhaust chambers **42** which carry it away. This is a critical step in the reduction of physical defects on the preform **40**.

After the preform **40** is formed, the process is shut-down and the preform **40** is

15 removed to an environmentally controlled storage area (not shown) where it will await consolidation process and, if needed, an intermediate chlorine treatment step. The consolidation of the porous preform **40** into a dense glass involves heating the preform to consolidation temperatures, typically 1200 to 1900°C with preferred values in a range from 1300 to 1700°C, in vacuum or at atmospheric pressure. Chlorine treatment involves heating

20 the porous preform **40** in chlorine gas, usually in the presence of an inert gas such as helium. Chlorine treatment is generally best at temperatures just prior to consolidation of the preform **40**, typically 900 to 1100°C. The high temperatures allow reaction of metal impurities to form volatile metal chlorides which are removed. Additionally, the chlorine removes OH from the glass structure. Dehydration of the porous preform prior to consolidation can also be

25 accomplished by exposing the porous preform to a fluorinating gas, such as CF_4 or SiF_4, usually in the presence of an inert gas such as helium.

For applications which require low thermal expansion, the SiO_2-TiO_2 glass formed by the process above has TiO_2 content in a range from 2 to 12% by weight. The weight percent of TiO_2 in the glass can be adjusted by changing the amount of titanium precursor **18**

30 delivered to the deposition burners **28**. The consolidated preform made by the process above can be finished and used as a mask blank for EUV lithography. Finishing may include cutting the preform into a desired shape, polishing the surface of the preform, and cleaning the preform. Figures 2 and 3 show a mask blank **46** having a planar top surface **48** and a planar bottom surface **50**. A consolidated preform produced by the process above can be cut

as necessary to form the mask blank **46**. A mask for EUV lithography can be formed by depositing alternating layers of reflective coating, *i.e.*, Mo/Si or Mo/Be, on the glass substrate and depositing an absorber, *e.g.*, Al or Si, on the multilayer reflective coating.

Dry SiO_2-TiO_2 glass can be used in fabricating optical elements for infrared transmission in the 700 to 1600 nm wavelength range, and more specifically in the 1200 to 1600 nm wavelength range. Dry SiO_2-TiO_2 glass can also be used in fabricating optical elements for deep-UV applications such as at 157 nm.

While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.